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15. SUPPLEMENTARY NOTES

16. ABSTRACT

Sampling for carbon monoxide for transportation impact studies is often accomplished by using air sampling bags. Manpower limitations often require storage of the samples for several days before analysis can be made. The primary purpose of this study is to determine the feasibility of replacing Scotch-Pak bag material (an aluminized polyester) with Tedlar bag material (a fluorinated hydrocarbon) for bag sampling purposes. The Scotch-Pak material which is currently being used is no longer manufactured and therefore a substitute (Tedlar) bag material was evaluated.

A secondary objective of this study was to examine the feasibility of analyzing the bag samples for hydrocarbon concentrations. This included an analysis to determine if any change in the reactive hydrocarbon (RHC) concentration or carbon monoxide concentration of bag samples occurred with time, bag material, or environmental storage conditions.

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STATE OF CALIFORNIA
DEPARTMENT OF TRANSPORTATION
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TRANSPORTATION LABORATORY

December 1975
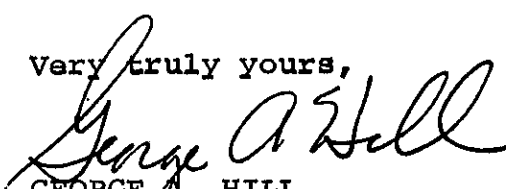TL No. 657082

Mr. C. E. Forbes
Chief Engineer

Dear Sir:

I have approved and now submit for your information this interim
research project report titled:

A FEASIBILITY STUDY OF TEDLAR BAG SAMPLING FOR

CARBON MONOXIDE AND HYDROCARBON ANALYSES

Study made by . . . . Environmental Improvement Branch

Under the Supervision of . . . . . E. C. Shirley, P. E.

Principal Investigator . . . . . . A. J. Ranzieri, P. E.

Report Prepared by . . . . M. D. Batham, P. E.

Assisted by . . . . D. J. Ames

Very truly yours,

GEORGE A. HILL
Chief, Office of
Transportation Laboratory

Attachment

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ACKNOWLEDGEMENTS

The work required for this study was performed by the Transportation Laboratory of the California Department of Transportation. This report was written by Michael D. Batham, Associate Air Sanitation Engineer and Donald J. Ames, Assistant Physical Testing Engineer, under the supervision of Andrew J. Ranzieri and Earl C. Shirley. Special acknowledgement is given Mr. Charles Frazier of the Transportation Laboratory for his assistance with the Tenet time share computer analysis of the data. Also special acknowledgement is given to Mr. Norman Baker and his staff of District 03 Environmental Planning Branch for their assistance in obtaining data for this study.

The contents of this report reflect the views of the Transportation Laboratory which is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the State of California. This report does not constitute a standard, specification, or regulation.

INTRODUCTION

The California Department of Transportation (Caltrans) is involved
with an air monitoring program in order to assess the regional
impact of transportation systems on air quality. The present
program utilizes two air quality vans, one located in Los Angeles
and the other in the San Francisco bay area. Each van has the
capability of monitoring carbon monoxide (CO), hydrocarbons (HC),
oxides of nitrogen (NO_x), ozone (O_3), and particulates on a contin-
uous basis. To supplement these measurements an extensive air
sampling program using bag sampling techniques has been employed
for the last two years. Bag sampling is presently used for CO only.
Scotch-Pak, an aluminized polyester bag material, has been used
in the past due to its availability and inertness to CO. However,
Scotch-Pak is no longer manufactured and a suitable replacement
material must be considered. The primary objective of this study
was to examine the feasibility of using Tedlar, a fluorinated hydro-
carbon material as a substitute for Scotch-Pak. A second objective
of this study was to determine the feasibility of using Tedlar for
bag sampling hydrocarbons under field conditions.

All pollutant samples were taken from bottled synthetic mixtures
of hydrocarbons and carbon monoxide. The initial CO concentrations
ranged from 10 ppm to 30 ppm and the reactive hydrocarbon (RHC)
concentrations ranged from 2.8 to 3.0 ppm. The pollutant samples
were subjected to either room storage conditions or to ambient
storage conditions prior to analysis.

CONCLUSIONS

Based on the analyses of data for this study, the following conclusions were reached for bags filled with a mixture of synthetic air and the pollutant of interest.

1.   The concentrations of both carbon monoxide and reactive hydrocarbons are independent of

     .bag material used (Tedlar and Scotch-Pak)

     .bag storage time (up to 6 days)

     .environmental storage condition (room storage or
      ambient storage)

2.   Samples containing RHC or CO in synthetic air can feasibly be collected and stored in Tedlar bags for periods up to 6 days. During this period the bags may be stored in either a room or an ambient environment without significantly affecting the concentration of RHC or CO.

IMPLEMENTATION

Based upon this study, it was determined that Tedlar bag material
is a suitable substitute for the currently used Scotch-Pac
material when sampling for CO. Therefore, it is recommended
that Tedlar be used on all future CO bag sampling studies.

For hydrocarbons, it is recommended that an in-depth study be
conducted because this study used synthetic gases which do not
accurately simulate ambient air. This in-depth study should
be all inclusive and have a sufficient number of data points
to establish better statistical confidence. Ambient air samples
should be used and exposed to field temperature fluctuations
without direct sunlight exposure. This will simulate typical
field sampling procedures. Replication of the study should be
made for various ratios of ambient RHC and NO_x concentrations.
This type of detailed study must be made before field sampling
of RHC can be performed with any degree of accuracy.

BACKGROUND

Hydrocarbons

Natural background concentrations of atmospheric hydrocarbons (HC)
occur at a level of about 1.6 parts per million (ppm) by volume,
of which approximately 1.5 ppm is methane. However, urban
concentrations have reached maximum hourly values of 8-17 ppm
of total hydrocarbons (THC) with approximately half being methane[1].

Natural sources of nonmethane hydrocarbons are mostly from the
decomposition of organic material. Worldwide technological
sources of nonmethane hydrocarbons amount to only 8% of the natural
sources and include motor vehicles (49%), industrial processes (16%),
organic solvent evaporation (10%), forest fires (7%), solid waste
burning (5%), gasoline marketing (4%), and other miscellaneous
sources[2].

Total hydrocarbon concentration measured in ambient air is
meaningless unless the methane concentration is also measured.
Although there are over 80 known hydrocarbon compounds, with
varying degrees of reactivity, in ambient urban air, methane
is said to represent the main portion of the non-reactive
hydrocarbons.

It is the reactive (nonmethane) portion of the THC which is of
concern in air quality. Although there is little evidence to
indicate direct health effects of the hydrocarbons in the ambient
air[3], hydrocarbons play an essential role in the formation of
photochemical smog. This was considered by the Environmental
Protection Agency (EPA) in setting the maximum allowable con-
centration for the National Ambient Air Quality Standards. EPA
found that an early morning RHC concentration of 0.3 ppm would
likely produce a photochemical oxidant concentration of 0.10 ppm[1].
Since the one hour oxidant concentration standard was set at 0.08
ppm, the RHC standard was set at 0.24 ppm.

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Carbon Monoxide

Carbon monoxide (CO) is a colorless, odorless gas which is
generated primarily by the combustion of fossil fuels in
automobiles. Natural background concentrations of (CO) are
estimated to be about 0.1 ppm while urban concentrations range
from 2 to 40 ppm with short-term peaks as high as 100 ppm
where automobiles are heavily concentrated[4]. Studies made
by the Transportation Laboratory in measuring the temporal and
spatial distribution of CO along freeways in Los Angeles have
also confirmed these figures[5].

The primary health concern of CO is due to its direct toxic
effect on humans. Red blood cells, each of which are made up
of many millions of molecules of hemoglobin, normally exchange
carbon dioxide (CO_2) for oxygen (O_2) through the alveolar cells
of the lung. However, the hemoglobin molecule has an affinity
for CO which is 210 times greater than it is for O_2. Thus a
CO molecule is acquired by the hemoglobin in place of an O_2
molecule and is called carboxyhemoblogin (COHb).

An exact threshold effect from CO is difficult to measure, but
as little as 2% COHb can affect a person's ability to estimate
time intervals[6]. At about 5% COHb, visual sensitivity in the
dark is reduced. A 5% COHb is the approximate level maintained
in the blood when a person is exposed to 9 ppm CO for 8 hours
or 35 ppm for 1 hour, the current Federal standard. It has been
observed that smoking one package of cigarettes a day will produce
COHb levels of about 5%[3].

EXPERIMENTAL PROCEDURES

The purpose of the study was to determine if any of the following variables significantly changed the initial sample concentrations of carbon monoxide and/or hydrocarbons: 1) Bag material, 2) time, and 3) initial sample concentration. Ambient storage vs. room storage conditions were considered for all variables mentioned above.

Two bag materials were used in the study, both of which are considered inert to most ambient gaseous pollutants. "Scotch-Pak", an opaque aluminized polyester product, was tested against "Tedlar", a transparent material made from fluorinated hydrocarbons. The bags made of Tedlar were transparent. This allowed the gases in them to be subjected to ultra-violet radiation when placed in ambient conditions.

The bags were filled with two different synthetic mixtures of gases. These gases were obtained from cylinders supplied by Bert Lovell and Sons of Sacramento and had previously been calibrated by the Air and Industrial Hygiene Laboratory of the California Department of Health, Berkeley. One mixture contained 31 ppm CO and 4.9 ppm THC (2.8 ppm RHC and 2.1 ppm methane) in dry nitrogen. The other mixture contained 10 ppm CO and 7.2 ppm THC (3.0 ppm RHC and 4.2 ppm methane) in dry nitrogen. The bags were filled directly from the gas cylinders with a section of teflon tubing. They were also emptied by means of a teflon tube connected to the analyzer. Teflon tubing was used because of its inert characteristics. The hydrocarbon measurements were made with a Bendix Model 8201 Flame Ionization Detector (FID) Gas Chromatograph. This instrument is accurate to within 1% of full scale or ±0.1 ppm. All CO measurements were made with a Beckman 315(A) long path nondispersive infrared analyzer (NDIR) which has an accuracy of 1% of full scale or

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±0.5 ppm. Each bag tested was new and had no preconditioning.
The bags were filled within approximately an one-hour period.
Half of the bags were stored outside for sunlight exposure
(temperature range 50°-90°F) and the other half were stored
inside at room temperature (65°-75°F).

See Figure 1 for a schematic of the sampling procedure used. The
concentration ranges for RHC and CO used in this study were based
on actual field measurements made by the Transportation Laboratory
along freeways in the Los Angeles area[5]. Therefore, the con-
centrations selected are representative for typical CO and RHC
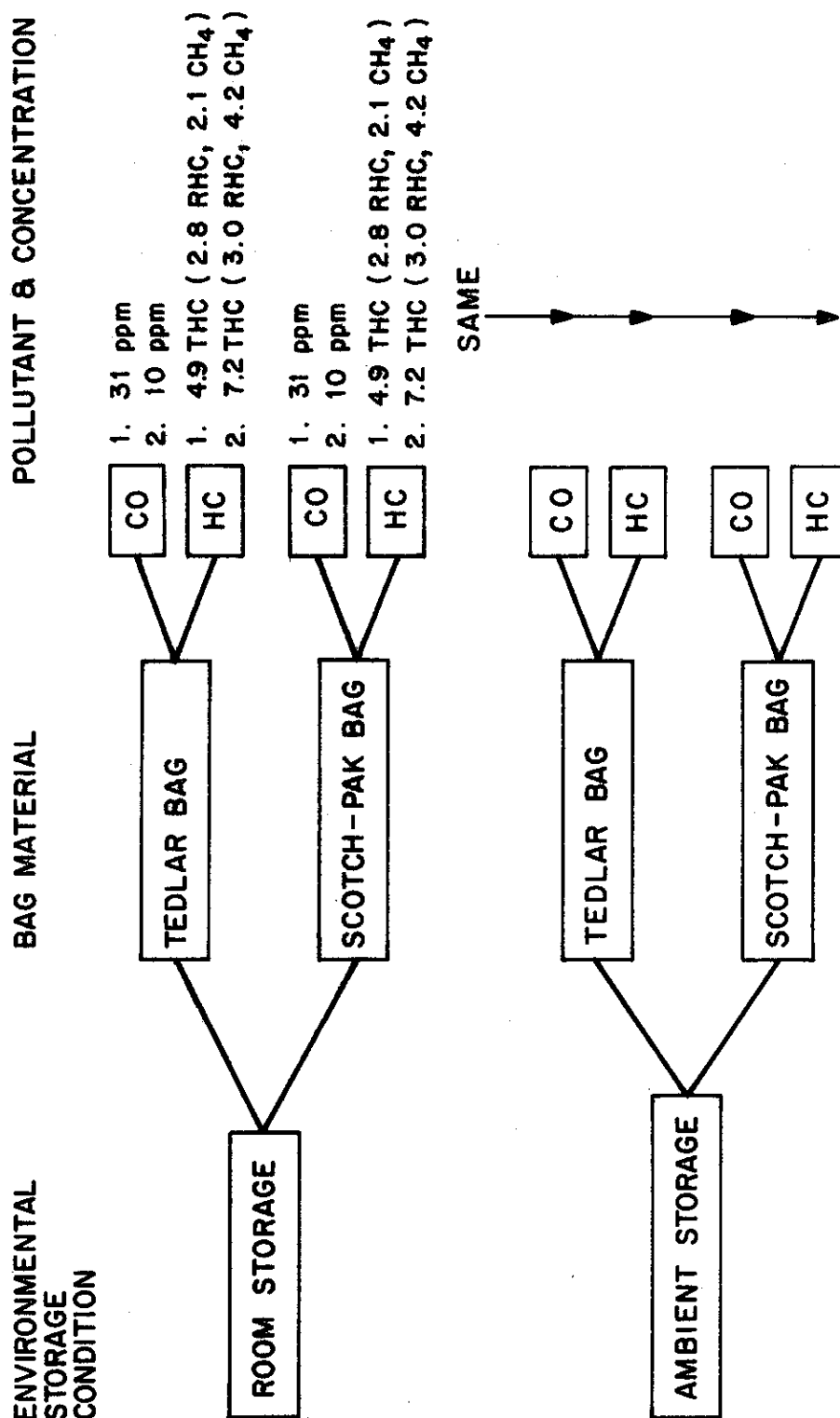levels that exist in large urban areas.

POLLUTANT & CONCENTRATION

ENVIRONMENTAL STORAGE CONDITION

BAG MATERIAL

CO	1. 31 ppm 2. 10 ppm		
HC	1. 4.9 THC (2.8 RHC, 2.1 CH$_4$) 2. 7.2 THC (3.0 RHC, 4.2 CH$_4$)	TEDLAR BAG	ROOM STORAGE
CO	1. 31 ppm 2. 10 ppm		
HC	1. 4.9 THC (2.8 RHC, 2.1 CH$_4$) 2. 7.2 THC (3.0 RHC, 4.2 CH$_4$)	SCOTCH-PAK BAG	
CO	SAME → → → →		
HC		TEDLAR BAG	AMBIENT STORAGE
CO			
HC		SCOTCH-PAK BAG	

FIG. 1   SCHEMATIC OF SAMPLING PROCEDURE

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EXPERIMENTAL RESULTS

The experimental data obtained in this study are listed in Table 1. This table shows the reactive hydrocarbon (RHC) and carbon monoxide (CO) concentrations versus time for the two bag materials, the various initial concentrations, and storage conditions. The blank spots indicate where no measurement was made because one of the cylinders ran low on gas. The limited amount of gas restricted the total number of samples which could be analyzed. It was expected that the room storage condition would show an initial concentration change less than the ambient storage condition due to minimal temperature changes and no sunlight exposure. For this reason, these samples were not analyzed until the 48th hour of the study in order that a later concentration change might be detected.

Data followed by a "*" means these data points were estimated in order to provide a complete data matrix. The matrix must be complete in order to statistically analyze the results using regression analysis and analysis of variance. The missing data points were estimated by visual inspection and interpolation (averaging) of the surrounding data. The figures in the Appendix show the plots of the data so a visual check can be made to see how the concentrations varied with time.

TABLE 1
RHC AND CO CONCENTRATION VS. BAG STORAGE TIME

RHC DATA (PPM)

TIME (HOURS)

	0	2	4	6	8	10	22	24	28	48	54	70	77	125	142	168	172	196	384
C1HC SCOTCH AMB	3.0	3.0	3.0	3.1	3.1	3.1	3.0	3.0	2.9	3.0	3.2	3.0	2.7		3.0	2.9	3.9	3.1	3.4
C1HC SCOTCH ROOM	3.0	3.1				3.0*			3.0	3.0	3.0	3.0		3.1	2.6	3.0	3.0	3.0	3.2
C2HC SCOTCH AMB	2.8	2.8	2.8	2.8	2.8	2.7	2.7	2.8	2.7	2.6	2.7	2.5	2.4	2.4	2.6	2.3	2.4	2.3	2.8
C2HC SCOTCH ROOM	2.8	2.8	2.7	2.7	2.7	2.7	2.7	2.6	2.6	2.7	2.7	2.6	2.3	2.6	2.6	2.4	2.6	2.6	2.9
C1HC TEDLAR AMB	3.0	3.0	3.0	3.1	3.1	3.1	3.0	3.0	3.0	3.0	3.0	3.1	2.8	3.4	3.2	3.0	3.3	3.3	4.0
C1HC TEDLAR ROOM	3.0	3.1				3.0*			2.9	2.9	3.0	3.0	2.6	3.0	2.8	2.8	2.5	2.5	2.5*
C2HC TEDLAR AMB	2.8	2.7	2.7	2.6	2.7	2.7	2.7	2.7	2.7	2.7	2.8	2.7	2.5		2.8	2.7	3.0	2.8	3.6
C2HC TEDLAR ROOM	2.8	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.6	2.5	2.6	2.6	2.3	2.7	2.5*	2.4	1.1	2.4	2.9

CO DATA: (PPM)

TIME (HOURS)

	0	2	4	6	8	10	22	24	28	48	54	70	77	125	142	148	172	196	384
C1CO SCOTCH AMB	31	31	32	31	31	31	30	30	31	28	31	28	31	30	30*	30	30	31	31
C1CO SCOTCH ROOM	31	31				30*			30*	29	30	30		30	22	30	-	29	28
C2CO SCOTCH AMB	10	10	10	10	10	10	10	10	10	10	9.5	9.5	9.5		9.0*	8.0	8	7	8
C2CO SCOTCH ROOM	10	10	10	10	10	10	9	10	10	9.0	10	9	9	8	5	9	9	10	9
C1CO TEDLAR AMB	31	32	32	33	32	32	31	32	32	33	32	33	33	37	37	32	39	40	46
C1CO TEDLAR ROOM	31	32				30*			30*	29	30	30	29	37	28*	27	22	27	23*
C2CO TEDLAR AMB	10	10	11	11	11	11	11	12	12	12	14	14	15		16	17*	19	14	28
C2CO TEDLAR ROOM	10	10	10	10	10	10	10	9	10	9	9*	9	10		9*	9*	10	-	9

C1 = HIGHER CONCENTRATION

C2 = LOWER CONCENTRATION

ROOM = ROOM STORAGE CONDITION
AMB = AMBIENT (SUNLIGHT) STORAGE CONDITION

* ESTIMATED CONCENTRATION
(FOR COMPUTER STATISTICAL ANALYSIS)

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DISCUSSION OF THE RESULTS

From the beginning of the data analysis, plots were made of the measured CO and HC concentrations versus time so any temporal trends in the data would be noticed. It soon became apparent that the degradation, if any, was very small between sample analyses. Therefore, the time between sample analyses was lengthened so a longer total span of time could be covered. The CO data for the same time period also did not indicate any degradation. This was expected, based on results from previous unpublished CO bag studies made by the Air Quality Unit of the Transportation Laboratory[5].

The four statistical tests which were used to analyze the data are as follows: (1) Wilcoxon matched-pairs sign rank test, (2) t test, (3) analysis of variance, and (4) least squares linear regression analysis. It is important to keep in mind that a statistically significant difference may not be physically important and therefore, not significant from a practical point of view. The Wilcoxon matched sign test and t test were used to determine whether a significant difference in pollutant concentration existed between the bag materials at the five percent level of significance. The Wilcoxon test is a non-parametric test which considers the magnitude of the differences within pairs of data. The null hypothesis assumes there is no significant difference between the bag materials. The results of the Wilcoxon analyses are shown in Table 2.

TABLE 2

WILCOXON MATCHED PAIRS SIGN RANKED TEST

Do Not Reject Null Hypothesis	Reject Null Hypothesis	Unable to Apply Test (Less than 5 Differences in Data Pairs)
C1HC Ambient	C1CO Ambient	C1CO Room
C1HC Room	C2CO Ambient	C2CO Room*
C2HC Ambient		
C2HC Room		

*C2CO room: There were only 4 differences in 14 pairs of data which indicates that the null hypothesis would not be rejected.

The t test for paired data was also used to determine if a significant difference existed between the two bag materials. Table 3 shows results of the F test, t test, and t test for paired data. The F test was applied prior to using the t tests in order to determine if the variances of the samples were significantly different. The t test assumes that the variances are not significantly different. As seen in Table 3, the ClCO Room, ClHC Ambient and ClHC Room groups were the only cases in which a significant difference between pairs of data was not measured statistically. However, three of the five failures did not pass the F test which indicates that the t test cannot be applied to the data.

Next, the analysis of variance test was used in order to determine if any parameter such as bag material or environmental storage condition had any significant effect upon concentration during storage time. This analysis considered the following four variables: (1) time (random); (2) environment (fixed-either room or ambient); (3) concentration (random); and (4) material (fixed – either Scotch-Pak or Tedlar). Each of these variables were compared with the observed concentration and then with all possible combinations of the other variables in the following manner; where T, E, C, and M represent time, environmental condition, concentration and bag material respectively:

CT
CE
CM
CET
CMT
CMET

14

TABLE 3

Results of F Test, t Test and t Test for Paired Data

	Carbon Monoxide				Reactive Hydrocarbons			
	C1 Amb.	C1 Room	C2 Amb	C2 Room	C1 Amb.	C1 Room	C2 Amb.	C2 Room
348 Hr. Analysis								
F Calc	14.53*	1.25	25.45*	1.20	1.03	2.09	1.51	6.84*
F Table	2.22	2.85	2.40	2.51	2.28	2.98	2.26	2.34
t Calc.		0.37	1.12		0.55	2.12	2.06**	
t Table		2.11	2.51		2.11	2.23	2.03	
Paired t Calc.		1.08		2.28**	0.63	1.83	2.12**	
t Table		2.37		2.16	2.11	2.23	2.11	
168 Hr. Analysis								
F Calc.	1.57		51.49*	1.18			3.36*	
F Table	2.48		2.69	2.69			2.55	
t Calc	4.45**			0.43				
t Table	2.15			2.20				
Paired t Calc.				1.83				
t Table				2.21				

* Fails the F test at 5% level of significance and therefore the corresponding t test is not valid.

**Fails the t test at 5% level of significance. The sample must pass all three of the above tests in order to conclude that there is no significant difference between the two bag materials.

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F-ratios were calculated at the 5% level of significance. No
significant F-ratios were obtained by comparing concentration with
the other variables. Statistically this means that, at the 5%
level of significance, the concentrations (both CO and HC) are
independent of time, bag material and environment.

Finally, linear regression analyses were applied because visual
inspection of graphs of the data indicated a linear relationship
between concentration and time. The data were analyzed twice:
once to compare all data (0-384 hours) and once to compare the
first 148 hours or 6 days. The six day analysis was made because
under normal conditions ambient bag samples would never be kept
more than 6 days. However, since the data were available, an
analysis was also made for 16 days (364 hours). There was
actually very little difference between the 6 day analysis and
the 16 day analysis. Table 4 is a summary of the 6 day regression
analysis. CO had five significant F-ratios and HC had three. The
greatest slope for CO was 0.044 ppm per hour increase or approximately
a one ppm increase per day for the low (10 ppm) concentration.
This change occurred using the Tedlar bag under ambient conditions.
The only significant slope for the RHC samples was a 0.0087 ppm/hr
or 0.21 ppm increase per day using the Scotch-Pak bags under
ambient conditions. This change was approximately a 7% increase
per day over the original RHC concentration and appears to be
significant when compared to the Federal Air Quality Standard
of 0.24 ppm. However, typical ambient concentrations of RHC as
measured by Caltrans in the Los Angeles Basin are on the order of
10 times the Federal Standard. In this light, the daily concentration
change appears somewhat less significant. Also, normal bag sampling
does not expose the samples to sunlight. The maximum change in
RHC concentration observed under room conditions was an insignificant
0.04 ppm decrease per day.

TABLE 4

LINEAR REGRESSION ANALYSIS OF 6-DAY CO AND RHC DATA

	F COMPUTED	F CRITICAL	F COMPUTED >FCRIT ?	N	EQUATION*	EQUIVALENT PPM CHANGE PER DAY
C1CO SCOTCH AMBIENT	2.67	4.67	NO	15	$Y=30.8-.0103X$	--
C1CO SCOTCH ROOM	2.39	5.99	NO	8	$Y=30.9-.0265X$	--
C2CO SCOTCH AMB	111.61	4.75	YES	14	$Y=10.1-.0126X$	0.3 DECREASE
C2CO SCOTCH ROOM	19.03	4.60	YES	16	$Y=10.2-.0192X$	0.5 DECREASE
C1CO TEDLAR AMBIENT	12.96	4.60	YES	16	$Y=31.6+.0241X$	0.6 INCREASE
C1CO TEDLAR ROOM	32.46	6.61	YES	7	$Y=31.4-.0296X$	0.7 DECREASE
C2CO TEDLAR AMB	102.99	4.75	YES	14	$Y=10.6-.0444X$	1.1 DECREASE
C2CO TEDLAR ROOM	3.50	4.96	NO	12	$Y=10.0-.0087X$	--
C1HC SCOTCH AMBIENT	1.922	9.07	NO	15	$Y=3.04-.00084X$	--
C1HC SCOTCH ROOM	1.75	5.59	NO	9	$Y=3.06-.00115X$	--
C2HC SCOTCH AMB	10.34	4.60	YES	16	$Y=2.93-.00873X$	0.21 DECREASE
C2HC SCOTCH ROOM	10.69	4.60	YES	16	$Y=2.72-.00169X$	0.04 DECREASE
C1HC TEDLAR AMBIENT	1.97	4.60	NO	16	$Y=3.01+.00087X$	--
C1HC TEDLAR ROOM	2.37	5.32	NO	10	$Y=3.00-.00128X$	--
C2HC TEDLAR AMB	0.04	4.67	NO	15	$Y=2.69+.00008X$	--
C2HC TEDLAR ROOM	8.58	4.67	YES	15	$Y=2.70-.00183X$	0.04 DECREASE

*Y(CONCENTRATION, PPM)
X(TIME, HOURS)

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In summary, the statistical analyses of the data indicated that the concentrations of both CO and RHC are independent of bag materials tested, storage time and environmental storage condition. This study should be repeated by an in-depth study which uses actual ambient air samples. These ambient samples would contain various reactive pollutants which might cause reactions within the samples. This would simulate actual field conditions.

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APPENDIX

GRAPHICAL PLOTS OF DATA

20
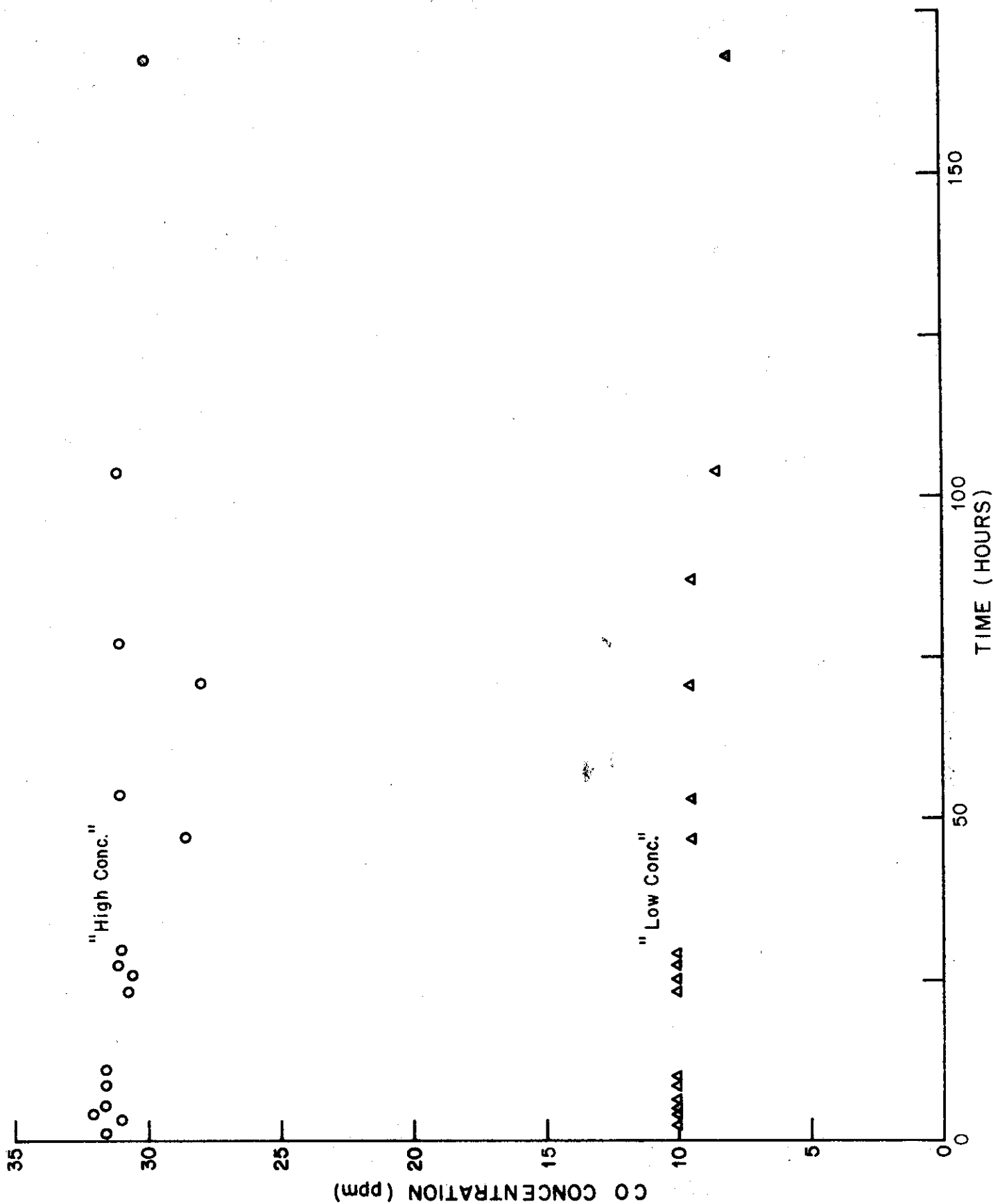
FIG. 2 CO CONCENTRATION VS TIME – "SCOTCH-PAC" BAG-AMBIENT CONDITION

21
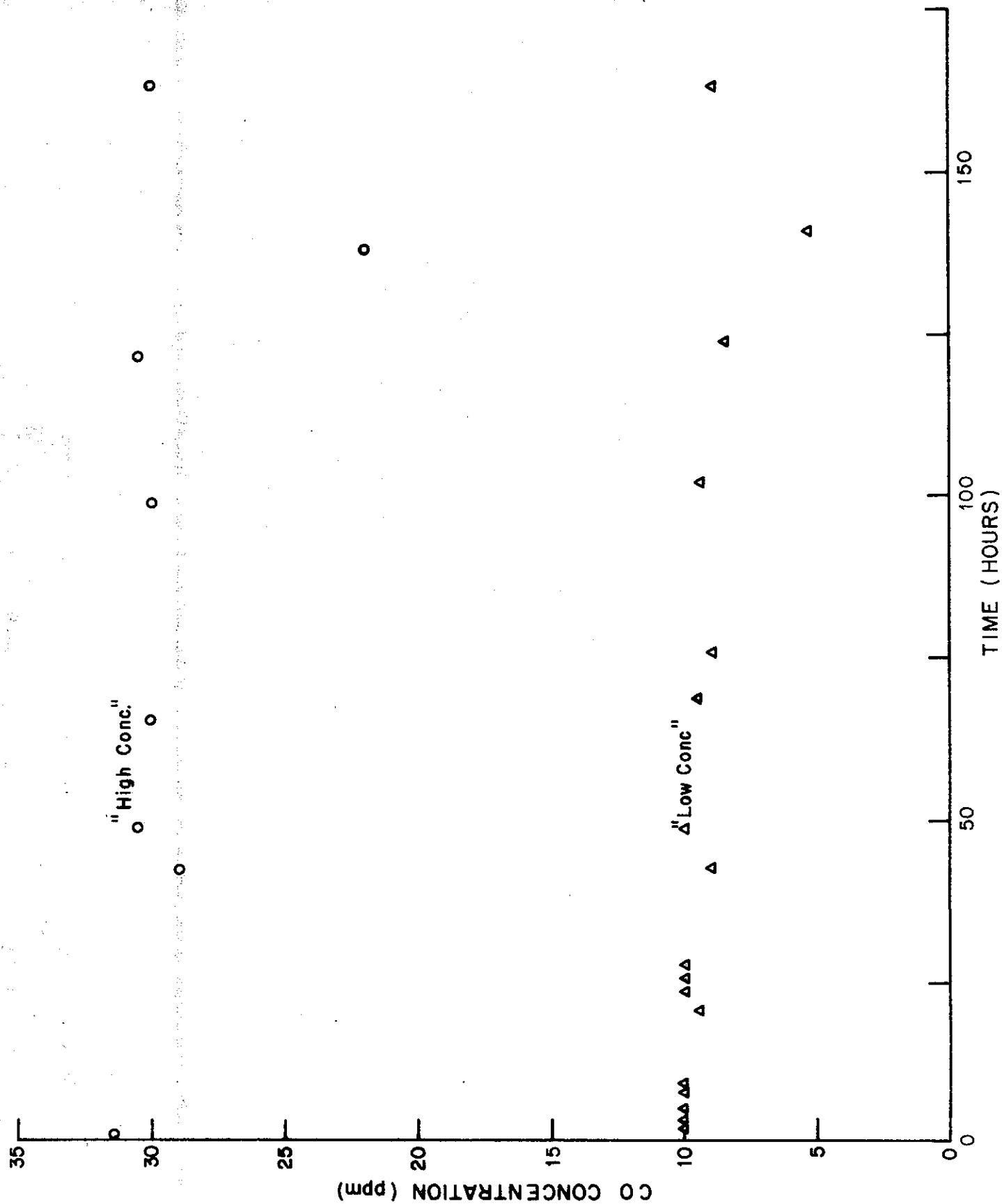
FIG. 3 CO CONCENTRATION VS TIME − "SCOTCH-PAK" BAG − ROOM CONDITION
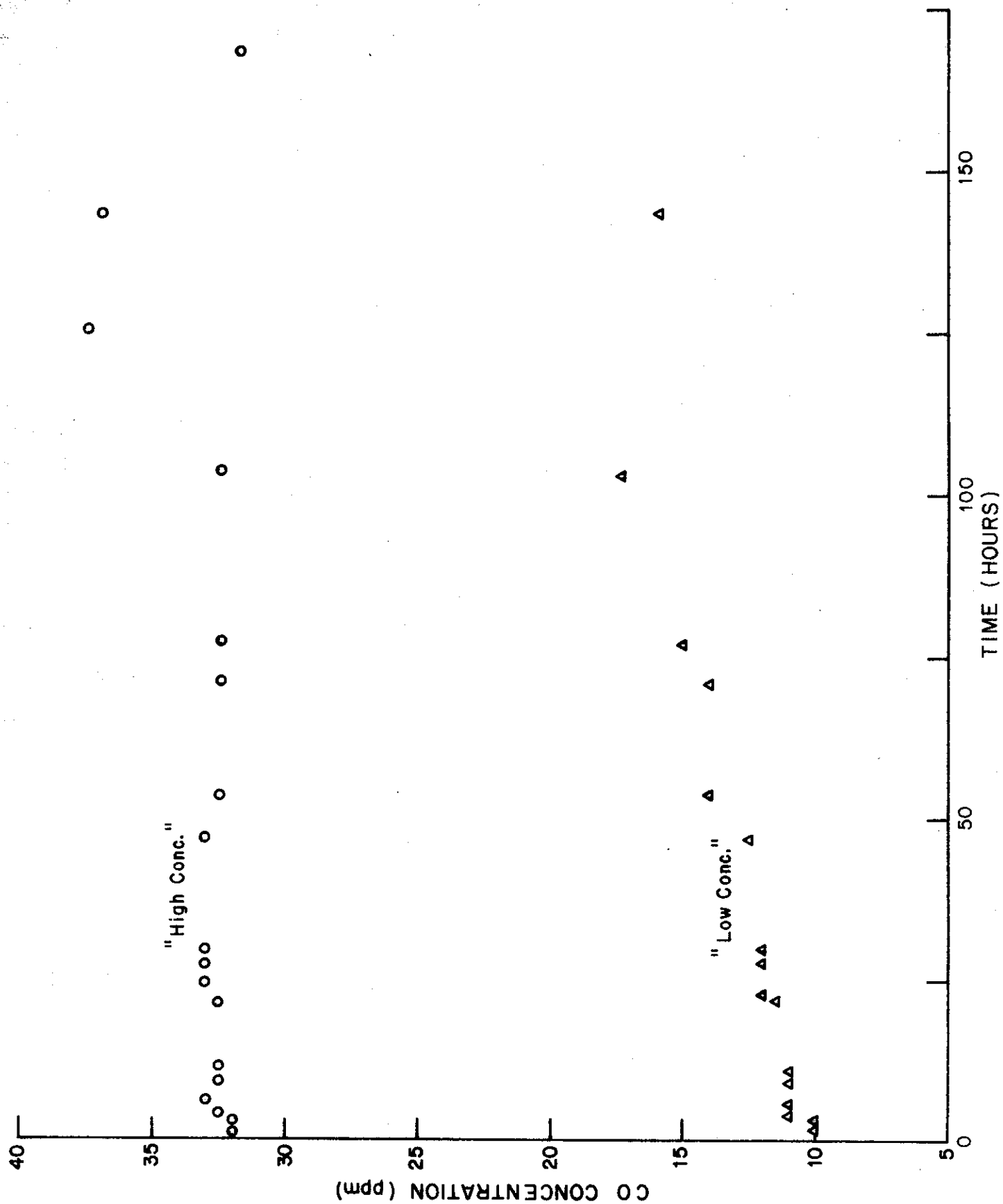
FIG. 4 CO CONCENTRATION VS TIME — "TEDLAR" BAG-AMBIENT CONDITION

23
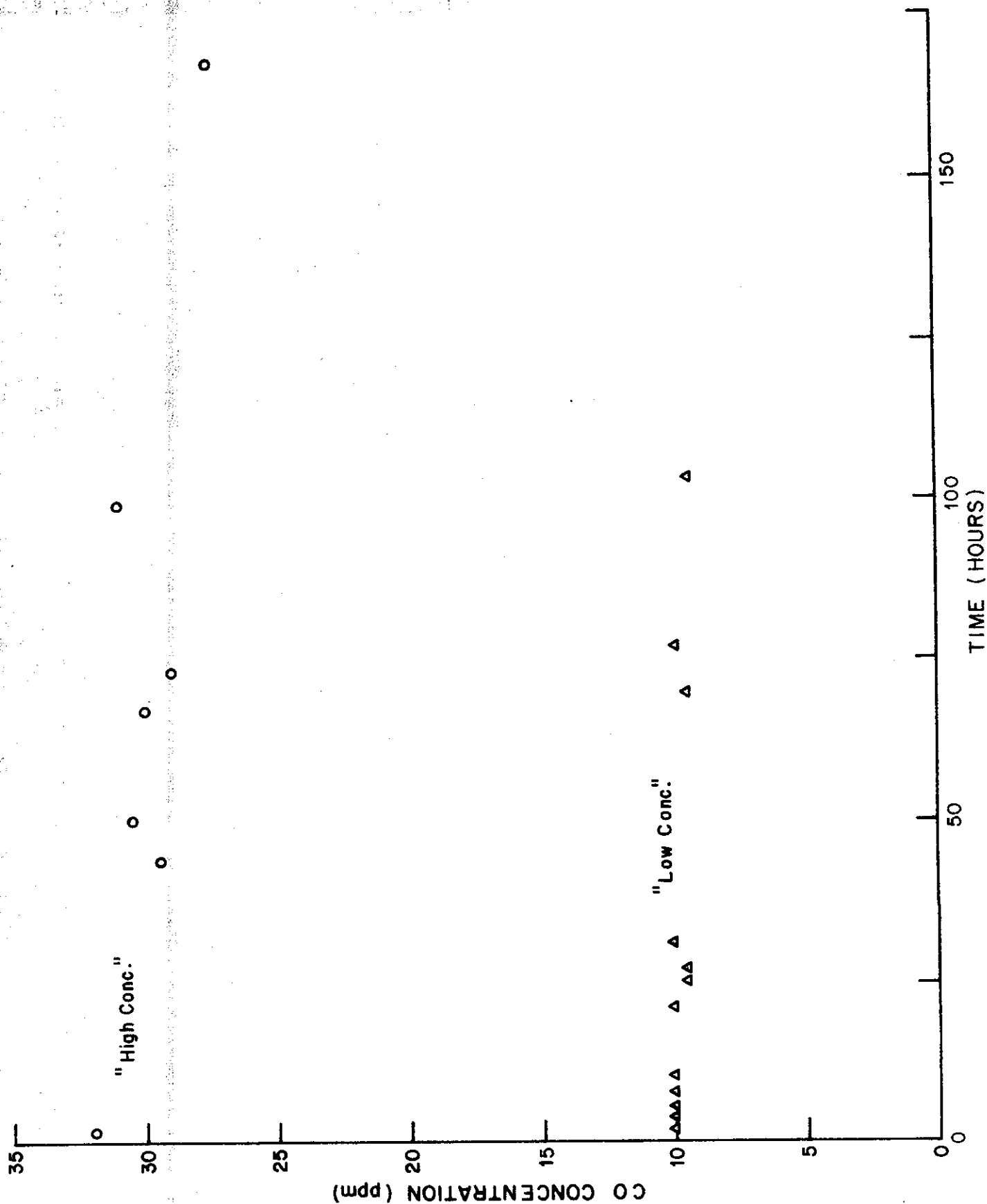
FIG. 5 CO CONCENTRATION VS TIME - "TEDLAR" BAG - ROOM CONDITION

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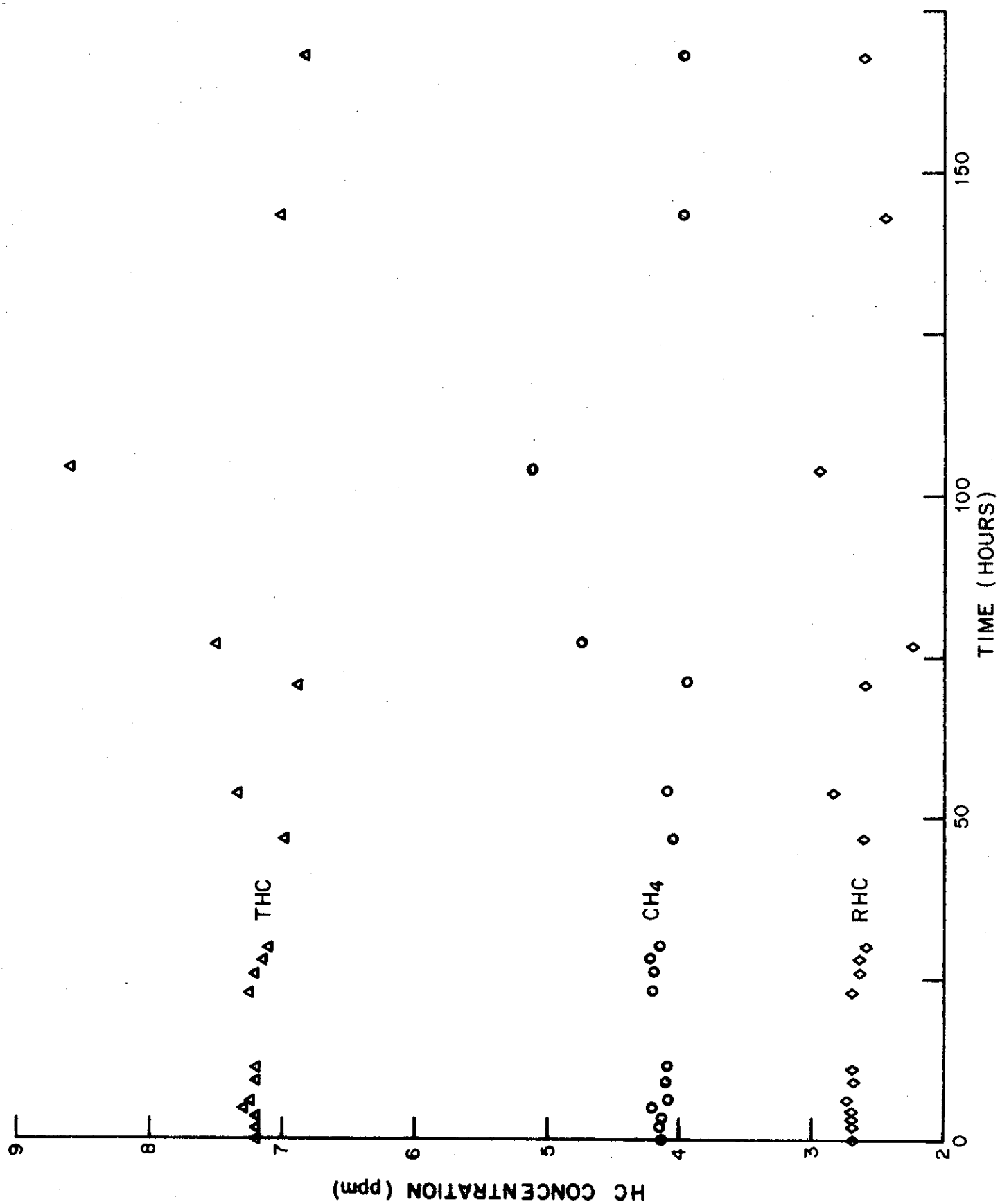
FIG. 6 HIGH HC CONCENTRATION VS TIME – "SCOTCH-PAC" BAG-AMBIENT CONDITION
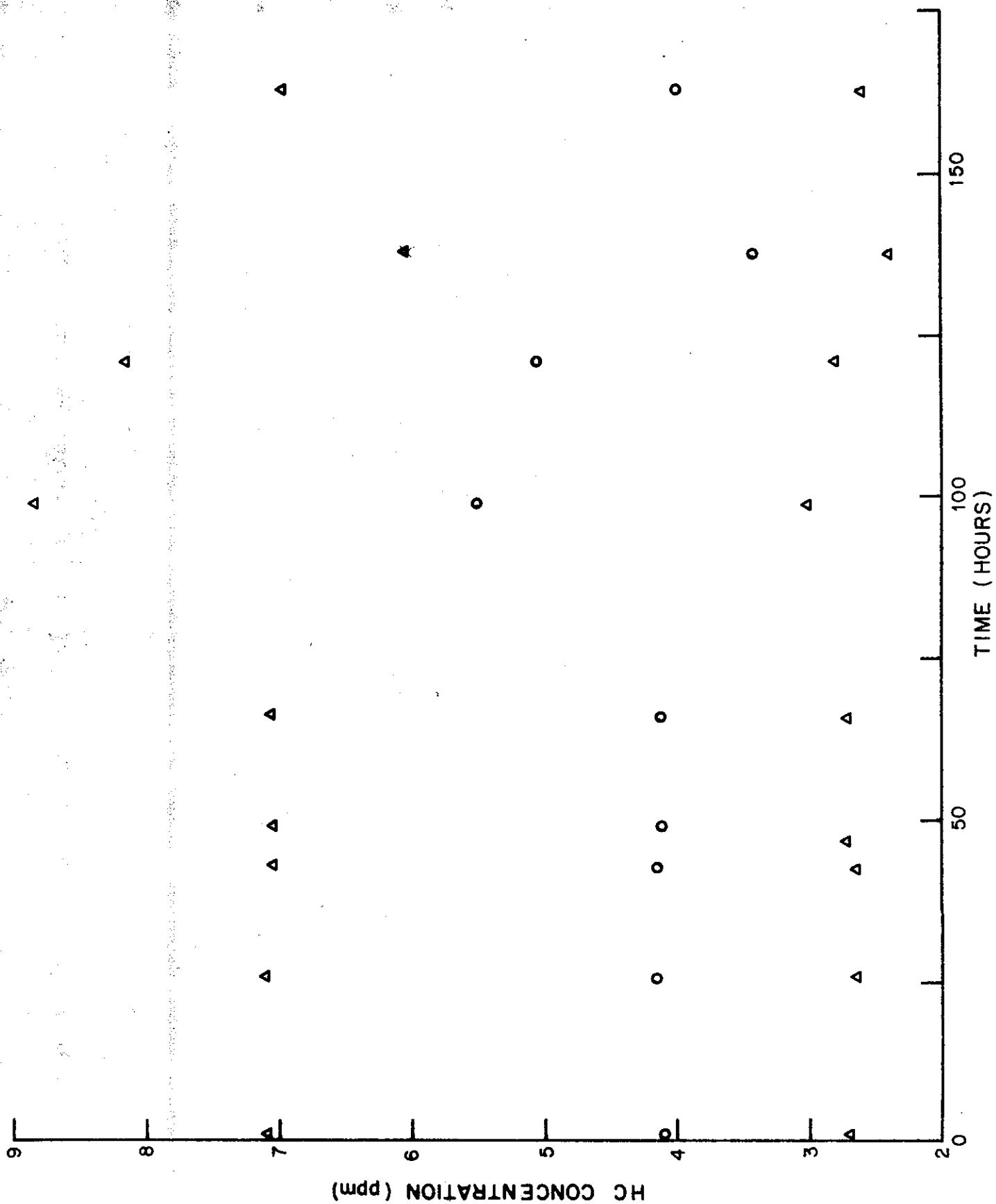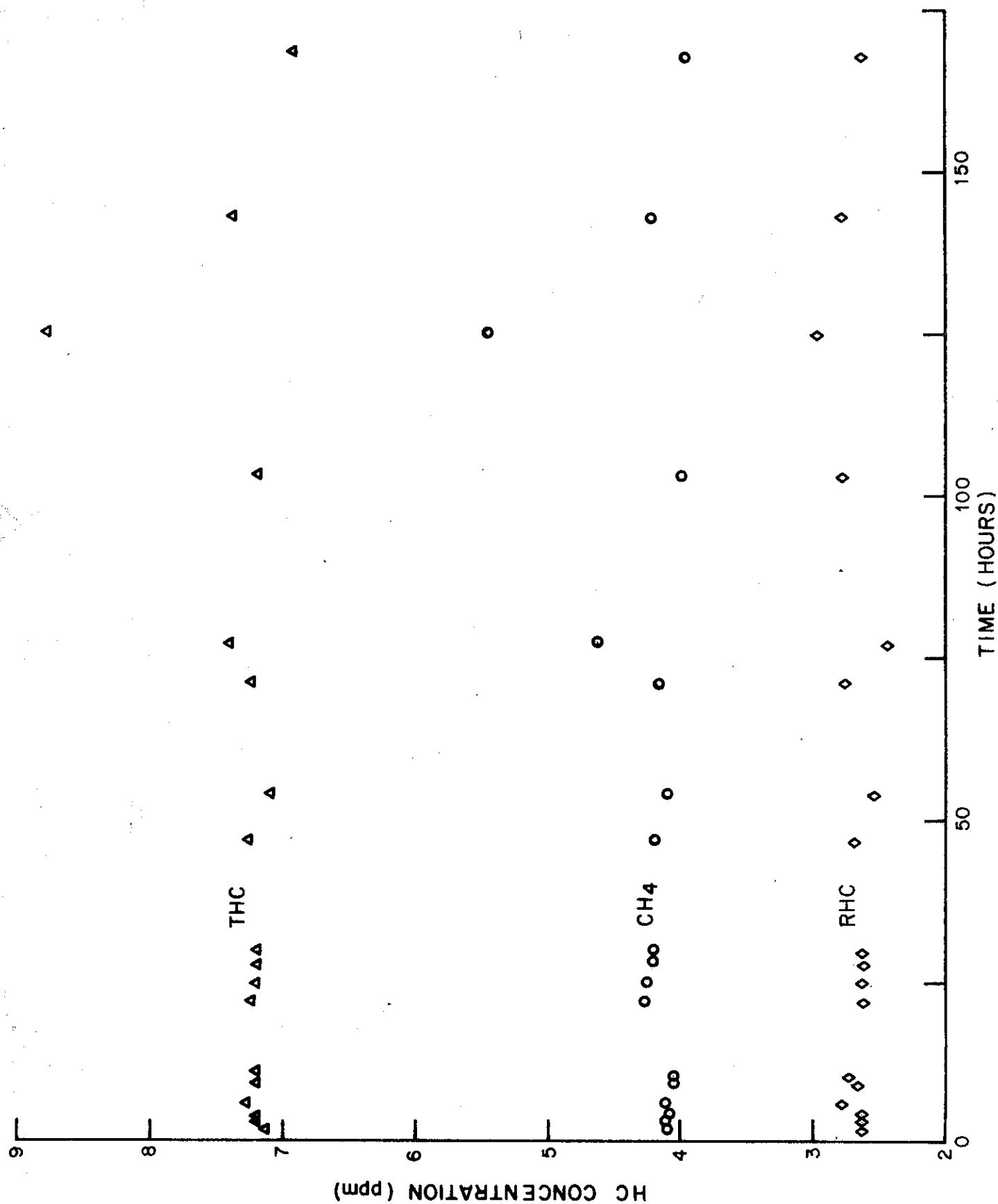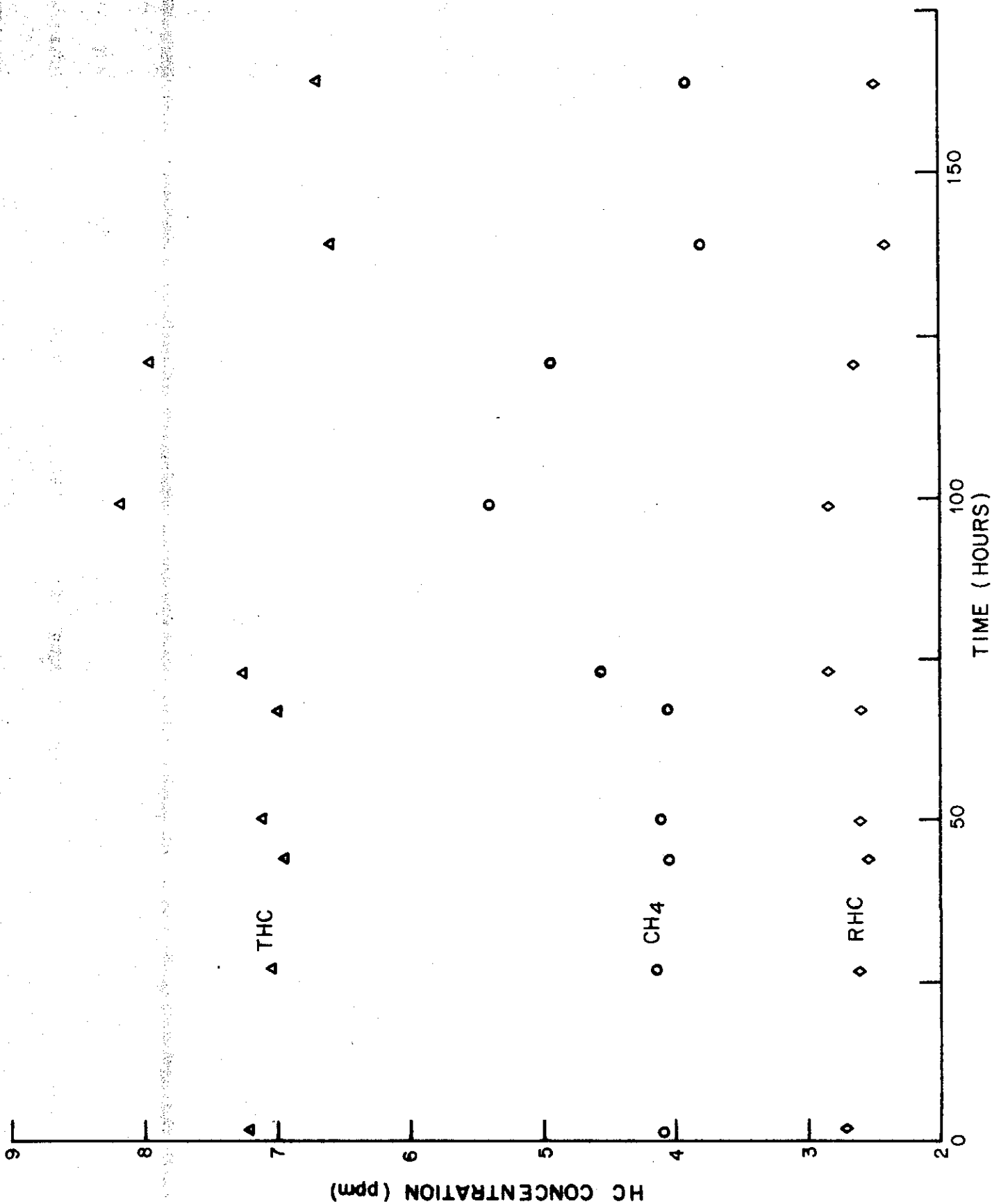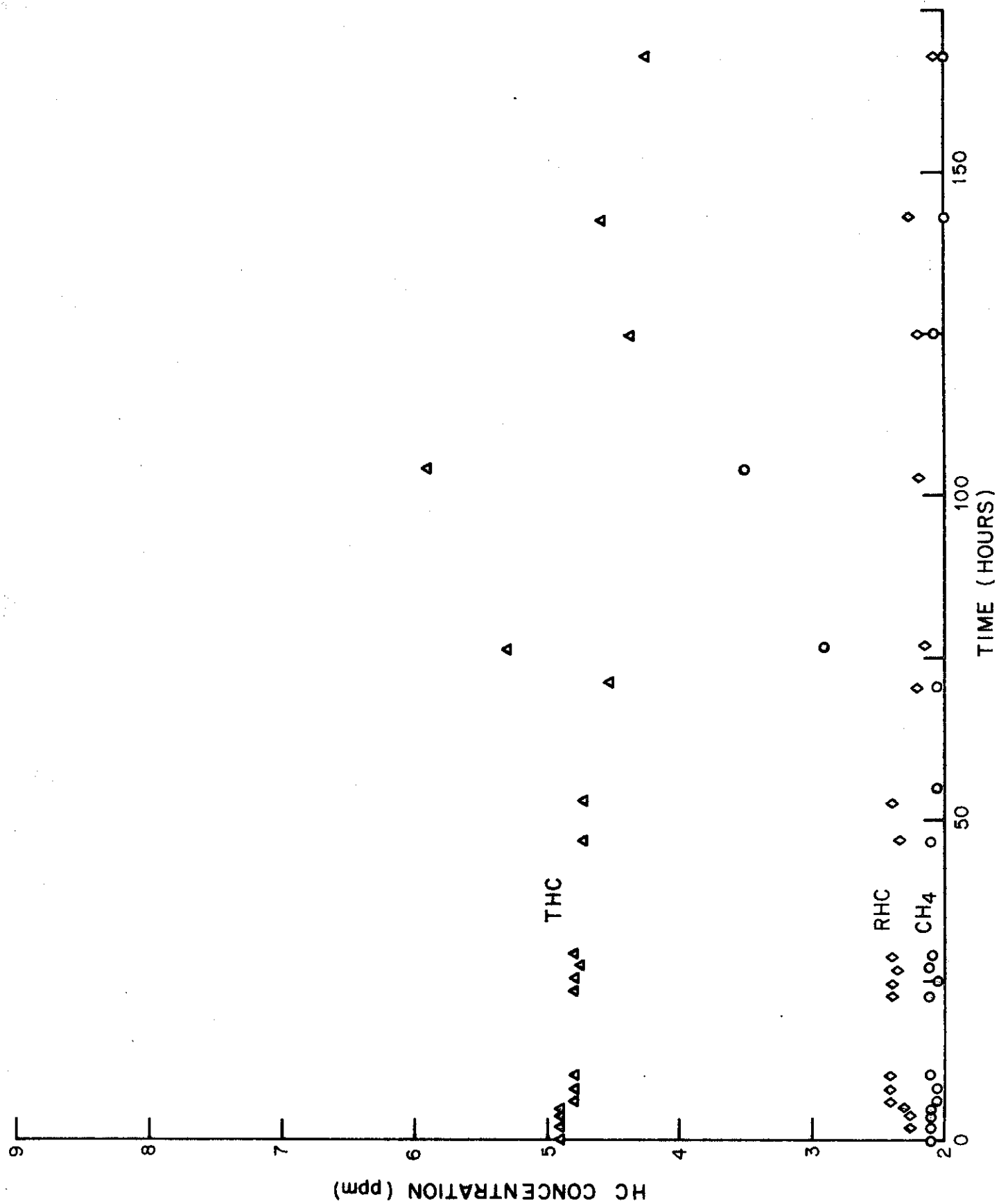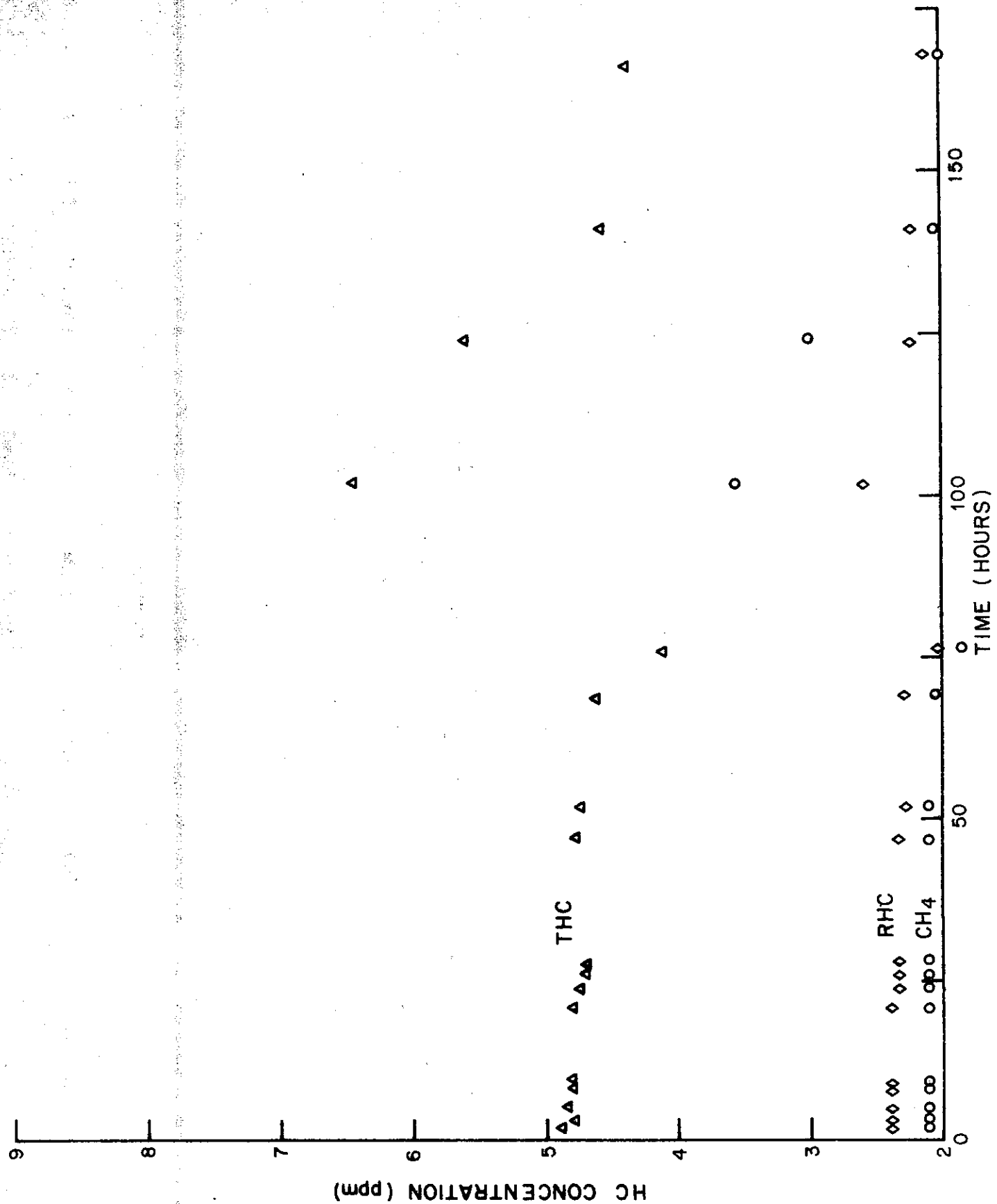
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FIG. 7 HIGH HC CONCENTRATION VS TIME – "SCOTCH-PAK" BAG – ROOM CONDITION

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FIG. 8 HIGH HC CONCENTRATION VS TIME—"TEDLAR" BAG-AMBIENT CONDITION

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FIG. 9 HIGH HC CONCENTRATION VS TIME – "TEDLAR" BAG – ROOM CONDITION

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FIG. 10 LOW HC CONCENTRATION VS TIME —"SCOTCH-PAK" BAG-AMBIENT CONDITION

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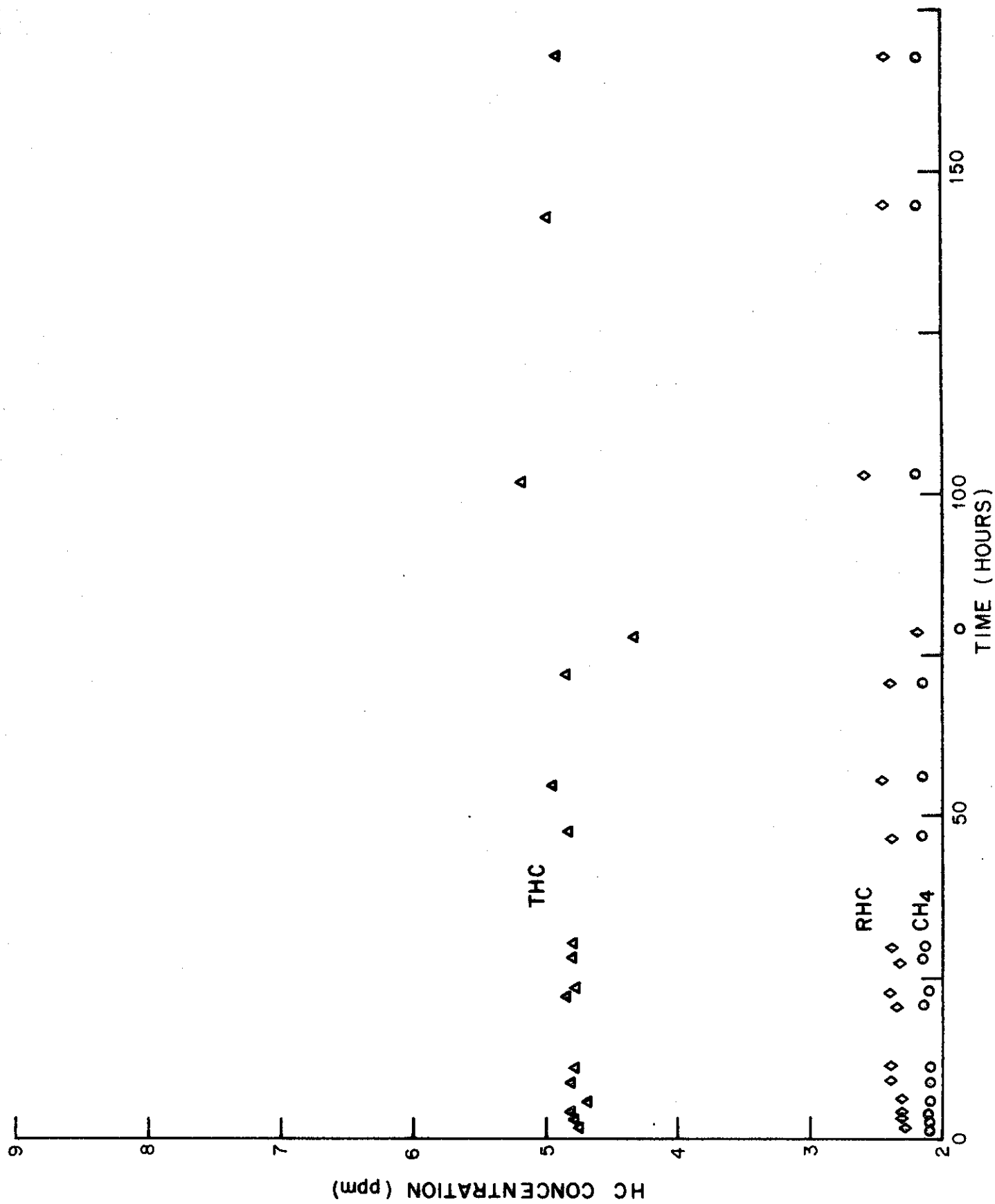FIG. 11 LOW HC CONCENTRATION VS TIME — "SCOTCH-PAK" BAG — ROOM CONDITION

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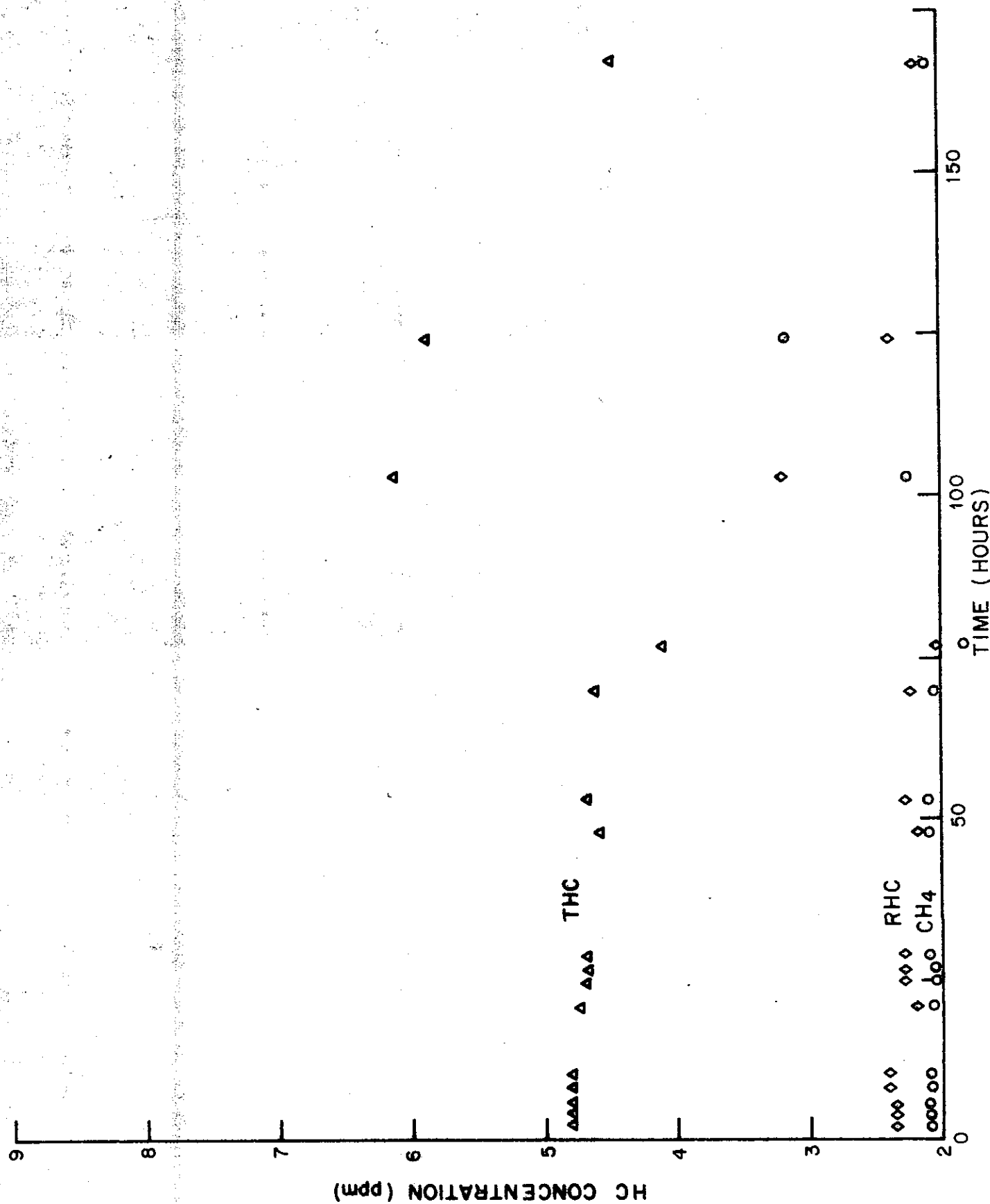FIG. 12 LOW HC CONCENTRATION VS TIME —"TEDLAR" BAG-AMBIENT CONDITION

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FIG. 13 LOW HC CONCENTRATION VS TIME — "TEDLAR" BAG – ROOM CONDITION

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